Ozone is a key to understanding atmospheric chemistry on Mars. Over 20 photochemical models of the martian atmosphere have been published, and O₃ abundance is often used as a benchmark for these models [1-3]. O₃ abundance has been inferred from instrumentation on several spacecraft, with the most complete coverage provided by Mariner 9 [3,4]. The Mariner 9 UV spectrometer scanned from 2100 to 3500 Å with a spectral resolution of 15 Å and an effective field of view of approximately 300 km² [4]. The only atmospheric absorption in the 2000-3000 Å wavelength region was previously assumed to come from the Hartley band system of ozone [4], which has an opacity of order unity at winter polar latitudes [3]. Therefore the amount of ozone was inferred by fitting this absorption feature with laboratory data of ozone absorption, as shown in Fig. 1 [4]. Mars O₃ shows strong seasonal and latitudinal variation, with column abundances ranging from 0.2 μm-atm at equatorial latitudes to 60 μm-atm over northern winter polar latitudes [4] (1 μm-atm is a column abundance of 2.689 × 10²⁴ molecules cm⁻²). However, the O₃ abundance is never great enough to significantly affect atmospheric temperatures [5] or surface temperatures and frost amounts [6]. Figure 2 shows some of the previously inferred O₃ abundances [7].

A radiative transfer computer model is used to reexamine the Mariner 9 UV spectra. Assuming a constant mixing ratio for O₃ and no chemical or radiative reaction interaction between O₃ and clouds/dust, Fig. 3 shows that when typical amounts of dust and cloud are present, significant underestimation of O₃ abundance occurs. A factor of 3 times as much O₃ is needed to generate the same spectrum the spacecraft would measure for a cloudy, dusty atmosphere as for a clear atmosphere. If the scattering properties of martian clouds and dust were well known, their appearance would not be a problem, as a model would be capable of retrieving the O₃ abundance. However, these properties are not well known, which raises doubts about the effectiveness of the UV reflectance spectroscopy technique for measuring O₃ abundance on Mars. The simulations shown in Fig. 3 are repeated for a range in solar zenith angle (50°-90°); ground albedo (0.3-0.8); altitude distribution of O₃; satellite viewing geometries; and cloud, dust, and O₃ abundances. A factor of 3 underestimation is typical, with greater underestimation for high ground albedo or high dust opacities. Even if scattering by clouds is properly accounted for (as previously done with Mariner 9 data reduction in [4]), masking by dust can easily result in factor-of-2 underestimation. Results are not strongly dependent on solar zenith angle.

Spatial and temporal variability in temperature and water vapor have been claimed to account for the scatter of the data points in Fig. 2 [8]. A decrease in temperature results in a decrease in water vapor, if saturated as expected at prevalent temperatures. A decreased water vapor abundance decreases the availability of odd hydrogen (H, OH, and HO₂), which converts CO and O into CO₂ catalytically, decreasing the abundance of O needed to form O₃. However, water vapor is a small source of odd hydrogen in the winter polar atmosphere compared to H₂, and may not account for most of the variability in Fig. 2 [3]. Masking by clouds and dust may also account for some of the observed O₃ variability, because the nature and opacity of the clouds and dust at winter polar latitudes change significantly spatially and temporally. As the maximum O₃ abundance resides near the surface [3], spacecraft must be able to observe through the entire cloud and dust abundance in order to measure the total O₃ column abundance. If reflectance spectroscopy is used, as on Mariner 9, then the cloud and airborne dust must be traversed twice, first by the incoming solar flux down to the surface, and then once again upon reflection from the surface out to the spacecraft. In addition, the large solar zenith angles at winter polar latitudes mean several times the vertical opacity of cloud and dust must be traversed. Indeed, part of the observed latitudinal variation in O₃ abundance in Fig. 2 may be due to the inability of the spacecraft to traverse the clouds and dust on the way to the surface.
to observe through the increasing effective optical depths as one goes poleward.

By using a photochemical model that included multiple scattering of solar radiation, Lindner [3] showed that the absorption and scattering of solar radiation by clouds and dust should actually increase \( O_3 \) abundances at winter polar latitudes. Hence, regions with high dust and cloud abundance could contain high \( O_3 \) abundances (heterogeneous chemistry effects have yet to be fully understood [2,9]). It is quite possible that the maximum \( O_3 \) column abundance observed by Mariner 9 of 60 \( \mu \)m-atm is common. In fact, larger quantities may exist in some of the colder areas with optically thick clouds and dust. As the Viking period often had more atmospheric dust loading than did that of Mariner 9, the reflectance spectroscopy technique may even have been incapable of detecting the entire \( O_3 \) column abundance during much of the Mars year that Viking observed, particularly at high latitudes. The behavior of \( O_3 \) is virtually unknown during global dust storms, in polar night, and within the polar hood, leaving large gaps in our understanding.

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The Effect of Polar Caps on Obliquity. B. L. Lindner, Atmospheric and Environmental Research, Inc., 840 Memorial Drive, Cambridge MA 02139, USA.

Rubincam [1] has shown that the martian obliquity is dependent on the seasonal polar caps. In particular, Rubincam analytically derived this dependence and showed that the change in obliquity is directly proportional to the seasonal polar cap mass. Specifically, Rubincam showed

\[
d \frac{d \psi}{dt} = 3 \times 10^{-10} \frac{M(t)}{M(0)} \text{ degrees/Earth year} \tag{1}
\]

where \( \psi \) is the obliquity and \( M \) is the mass of the seasonal polar caps, with time of \( \psi \) being the present. This expression assumes uniformly thick spherical caps with identical angular radii of 45°. However, even if a very different polar cap mass distribution is used, Rubincam estimates the total uncertainty in the constant in equation (1) to be less than a factor of 2. Using the current mass of the seasonal polar cap as typical over geologic time, Rubincam calculates that the amount that the obliquity would secularly change is only 1.4°. Considering that the current obliquity of Mars is 25°, Rubincam concludes that seasonal friction does not appear to have changed Mars’ climate significantly.

Using a computer model for the evolution of the martian atmosphere, Haberle et al. [2,3] have made a convincing case for the possibility of huge polar caps, about 10 times the mass of the current polar caps, that exist for a significant fraction of the planet's history. Given the large uncertainties in input parameters and in the model itself, the results must be regarded as speculative. Also, the Haberle et al. results have been unable to favor or rule out a large polar cap scenario vs. a small polar cap scenario.

Nonetheless, since Rubincam showed that the effect of seasonal friction on obliquity is directly proportional to polar cap mass, a scenario with a ten-fold increase in polar cap mass over a significant fraction of the planet's history would result in a secular increase in Mars' obliquity of perhaps 10° (using equation (1)). Hence, the Rubincam conclusion of an insignificant contribution to Mars' climate by seasonal friction may be incorrect. Furthermore, if seasonal friction is an important consideration in the obliquity of Mars, this would significantly alter the predictions of past obliquity as presented by Ward [4–6], Murray et al. [7], Ward et al. [8], Rubincam [9], Chao and Rubincam [10], Bills [11], Ward and Ruby [12], Touma and Wisdom [13], and Laskar and Robutel [14]. That in turn would significantly alter the predictions of past climate, which are based on obliquity predictions [15–20]. The mechanics of the polar cap system also depend on obliquity [21–26]. If obliquities were often much smaller than at present, that could have implications for past atmospheric composition [27].

Given the enormity of the implications, the effect of the polar caps on the obliquity of Mars should be given more attention and study. Perhaps further modeling of obliquity could be used to rule out the possibility of large polar caps for extended times, which would assist modeling of atmospheric evolution. Similarly, modeling of atmospheric evolution should be given more attention and study because of the implications for obliquity history, and therefore climate history.

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